

## 1,3-DIPOLAR CYCLOADDITIONS OF C-BENZOYL-N-PHENYLNITRONE INDOLE DERIVATIVES\*

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Received May 18th, 1981

Reaction of the title nitrone *I* with indole derivatives *IIa,b* gives the 1,3-addition product *IIIa,b*, its hydrogenated derivative *IVa,b*, and dehydrogenation products *VIa,b* and *VIIa,b* from transient product of 1,3-dipolar cycloaddition (*V*). Indole itself only gives cycloaddition products *VIc* and *VIIc*. Carbazole derivative *VIII* does not react due to sterical reasons. The reaction course is discussed on the basis of PMO theory. Structure of the products has been proved by <sup>1</sup>H and <sup>13</sup>C NMR, IR, UV, and mass spectra.

1,3-Dipolar cycloadditions with heterocycles as dipolarophiles are relatively rare. Our previous papers<sup>1-4</sup> dealt with the cycloaddition of C-benzoyl-N-phenylnitronone (*I*) with furane derivatives, benzofurane<sup>5</sup>, and furopyrrol derivatives<sup>5</sup>. This communication deals with reactions of indole derivatives *II* and *VIII* with nitrone *I*. The 1,3-dipolar cycloadditions of indoles have only been published so far with nitrile imines<sup>6-8</sup>. So, *e.g.*, the reaction with N-methylindole (*IIb*) gives the cycloaddition product 8-methyl-3a,8a-dihydropyrazolo[3,4-*b*]indole (*XI*) besides the non-cyclic product of 1,3-addition (3-indole derivative *XII*).

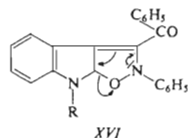
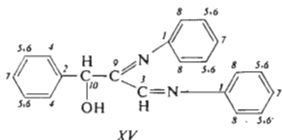
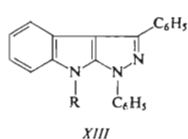
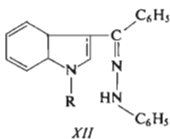
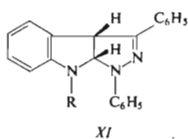
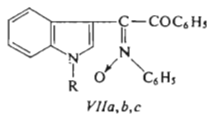
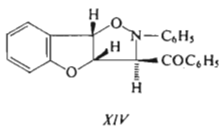
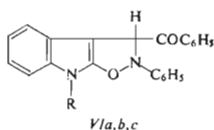
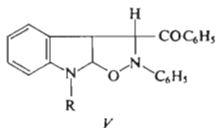
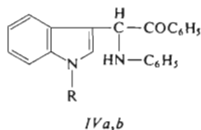
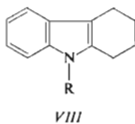
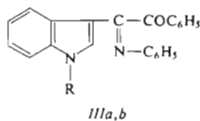
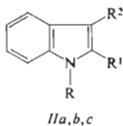
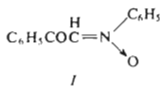
The cycloaddition of nitrone *I* with heterocyclic compounds was found<sup>1,4,5</sup> to be LUMO(*I*)-HOMO(heterocycle) controlled. The IP value found<sup>9</sup> for indole is 747.8 kJ mol<sup>-1</sup>, hence, indole and its derivatives should be considerably more reactive in 1,3-dipolar cycloadditions than benzofurane (835.6 kJ mol<sup>-1</sup>, ref.<sup>10</sup>) or furane (857.7 kJ mol<sup>-1</sup>, ref.<sup>5</sup>) because of the lowered energy difference between the frontier orbitals<sup>11-13</sup>. The cycloaddition reactions of indole described so far (be it with nitrile imines<sup>7</sup> or with dienophiles<sup>14</sup>) were always connected with subsequent attack of indoline NH group of the adduct formed by another reactant molecule, which led us to choice of N-butylindole<sup>15</sup> for the reactivity investigation. Besides protecting

\* Part *VIII* in the series 1,3-Dipolar Cycloadditions of Heterocyclic Compounds; Part *VII*: This Journal 46, 2421 (1981).

NH group of indole nucleus, the butyl group decreases the IP value in average by 38.6–48.2 kJ mol<sup>-1</sup> (ref.<sup>16</sup>), whereby the energy difference between the frontier orbitals of the reactants is further diminished. When the reaction mixture of nitron *I* and N-butylindole was left to stand at room temperature for 21 days, the products *IVb*, *VIb*, *VIIIb*, and *XV* were formed in the yields of 12, 9, 26, and 50% respectively. The product *VIIIb* exhibits the lowest  $R_F$  value in elutation with methanol, and its mass spectrum shows the molecular peak  $M^+$ :  $m/z$  396 with a fragment  $M^+$ –16 ( $m/z$  380) typical of fragmentation of azomethine oxides (nitrones)<sup>17</sup>. The 1:1-adduct should have the molecular peak with  $m/z$  value 398, hence the product *VIIIb* was obviously formed by dehydrogenation of cycloadduct *V*. The dehydrogenation splits off hydrogen atoms 3-H and 3a-H to give the derivative *XVI* which undergoes electrocyclic reaction with ring opening and restoration of the indole system *VIIIb*. Analogous electrocyclic ring opening was observed when monoadducts of *I* with furane<sup>3</sup> and furopyrrole derivatives<sup>5</sup> were dehydrogenated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. The reaction does not take place in the column by action of SiO<sub>2</sub>, as the product *VIIIb* is already present in the reaction mixture during the reaction (TLC). The suggested structure of *VIIIb* agrees fully with spectral data. The <sup>1</sup>H NMR spectrum contains a distinct triplet at the values  $\delta$  4.23 ppm corresponding to signals of a methylene group attached to nitrogen atom (N–CH<sub>2</sub>–). N-Butylindole (*IIB*) has the said triplet in the region at  $\delta$  4.00 ppm, which suggests restoration of aromatic indole system (ring current effect). The cycloadduct *V* should exhibit the triplet signals at about  $\delta$  3 ppm due to loss of heterocyclic system. Moreover, the <sup>1</sup>H NMR spectrum shows a sharp singlet at low field with the value  $\delta$  9.62 ppm corresponding to 2-H proton of indole skeleton. The said signal does not change its position on heating or addition of <sup>2</sup>H<sub>2</sub>O, which excludes OH or NH protons in accordance with IR spectrum: no absorption band is found in the region from 3 200 to 3 700 cm<sup>-1</sup>. The high value  $\delta$  9.62 ppm is due to shielding effect of negatively charged oxygen heteroatom in the nitron. Addition of shift reagent causes a distinct down-field shift ( $\Delta\delta > 2$  ppm), which is typical of protons in vicinity of nitron oxygen<sup>18</sup>. Also the UV absorption maximum (338 nm) of *VIIIb* agrees fully with distinct bathochromic shift of 3-indolynitron derivative as compared with N-butylindole itself ( $\lambda_{\max} = 290$  nm).

Product *VIb* was obtained in 9% yield as the substance with the greatest  $R_F$  value. Assignment of its structure was made difficult by the fact that it gives no molecular ion in mass spectrum. The <sup>1</sup>H NMR spectrum is relatively poor: it contains a multiplet of aromatic protons in the region 6.86–8.11 ppm, a singlet shifted considerably to lower field ( $\delta$  6.46 ppm), a triplet of methylene group adjacent to N atom, its value  $\delta$  3.96 ppm indicates preservation of ring current effect of indole nucleus. In the case of formation of the cycloadducts *V* the spectrum should have contained also two doublets of the 3a and 8a protons in the region  $\delta \sim 5.0$  and  $\sim 6.0$  ppm with the coupling constant  $\sim J = 10$  Hz, which was found in the case of the adducts

type XI (ref.<sup>6-8</sup>). Also value of chemical shift of N—CH<sub>2</sub> triplet should have been diminished in V by 0.5–1.0 ppm. The UV spectrum shows absorption maxima at 281



In formulae: a R = CH<sub>3</sub>, b R = n-C<sub>4</sub>H<sub>9</sub>, c R = H.

and 289 nm. The IR spectrum shows no vibrations in the region  $3\ 200-3\ 600\text{ cm}^{-1}$ , it only contains an absorption band of carbonyl group at  $1\ 691\text{ cm}^{-1}$ . The given spectral data and results of elemental analysis agree with the suggested structure of 2-phenyl-3-benzoyl-8-butyloxazolino[3,4-*b*]indole (*IVb*).

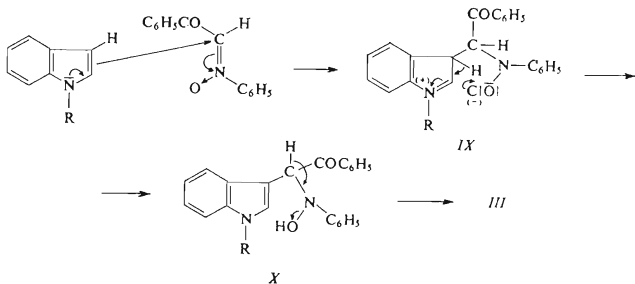
The compound *IVb* isolated in the yield of 12% exhibits mass spectrum with molecular peak  $M^{+}$ ,  $m/z$  382 and the fragment formed by loss of two hydrogen atoms  $m/z$  380. The IR spectrum contains absorption bands of  $\nu(\text{NH})$  and  $\nu(\text{CO})$  valence vibrations at  $3\ 408$  and  $1\ 692\text{ cm}^{-1}$ , respectively. The UV spectrum and the N—CH<sub>2</sub> triplet value  $\delta$  3.97 ppm prove that indole skeleton was maintained. In the <sup>1</sup>H NMR spectrum there are two doublets (with coupling constant  $J = 3.8\text{ Hz}$ ) at  $\delta$  6.32 and 4.93 ppm. The doublet at  $\delta$  4.93 disappears on addition of <sup>2</sup>H<sub>2</sub>O, hence, the signal is not due to the bridgehead protons in cycloadduct *V* but to CH—NH grouping in the molecule. Therefore, the compound *IVb* is assigned the structure of the 3-substituted indole derivative formed by hydrogenation of the 1,3-addition product *IIIb*. Formation of *IIIb* can be interpreted as electrophilic substitution of indole or 1,3-addition of nitronone *I* acting as electrophile in this case. The presumed course of 1,3-addition given in Scheme 1 can be viewed as a donor-acceptor interaction in which electron is transferred from the HOMO of indole derivative to the LUMO of nitronone *I* (ref.<sup>19</sup>). The CNDO/2 calculations carried out for indole<sup>8</sup> showed that the greatest AO coefficient in the HOMO is at the C<sub>(3)</sub> atom ( $C_2 = 0.38$ ,  $C_3 = 0.49$ ), so the products formed are the regioisomers type *III* (Scheme 1) and *V* or products of their subsequent reactions. The opposite regioisomerism of the 1,3-cycloaddition and 1,3-addition need not be taken into account, since the second dominant interaction HOMO(I)—LUMO(indole)<sup>8</sup> has no importance due to high  $\epsilon(\text{LUMO})$  value of indole. Compound *III* is formed by dehydration of *X* (which is similar to the 1,3-cycloaddition of *I* with 2-methyl- and 2-ethylfuran<sup>2</sup>) and further acts in the reaction mixture as a dehydrogenation agent for cycloadduct *V*, being transformed to the reduced form *IVb*. Splitting off of 3-H and 3a-H hydrogen atoms produces nitronones type *VII*, whereas the derivatives *VI* result from loss of 3a-H and 8a-H. There is no equilibrium between the products *VI* and *VII* in the reaction mixture, the said derivatives *VI* and *VII* being stable at 60°C for 40 h.

The structure *IVb* was also confirmed by dehydrogenation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at 60°C. Formation of *IIIb* was confirmed by interpretation of mass spectrum ( $M^{+}$ ,  $m/z$  380) and <sup>1</sup>H NMR spectrum: the latter lacks two doublets corresponding to signals of C—H and N—H groups. Also the IR spectrum lacks the absorption band in the region  $3\ 200-3\ 600\text{ cm}^{-1}$ .

Another substance isolated was the compound *XV* which does not contain valence vibrations of carbonyl group in its IR spectrum. The latter only shows absorption bands of OH group at  $3\ 568$  and  $3\ 225\text{ cm}^{-1}$  and C=C bond vibrations at  $1\ 598\text{ cm}^{-1}$ . The UV spectrum only contains an absorption maximum at 247 nm which indicates that the compound does not contain indole nucleus. The <sup>1</sup>H NMR spectrum shows

sharp singlet at  $\delta$  4.91 ppm and an aromatic multiplet in the region 6.50–7.95 ppm. The intensity ratio is 1 : 17. On the basis of analysis of the  $^{13}\text{C}$  NMR and mass spectra the compound can be assigned the structure *XV*. Its formation can be presumed to be the result of reduction with the hydrogen liberated from the transient cycloadducts *V*; the hydrogenated derivative of nitron *I* reacts with another molecule of nitron *I* to split off benzoic acid (its presence was proved in ref.<sup>1</sup>) and water. So far we have never isolate<sup>1-4</sup> the compound *XV*, because cycloadducts of furane, benzofurane, and furopyrrroles were stable under the reaction conditions used and did not undergo dehydrogenation.

The reaction of *I* with N-butylindole carried out at 60°C gave the 1,3-addition derivative *IVb* as the main product (45%) besides *VIIb* (13%) and *XV* (20%). The reaction of *I* with N-methylindole (*IIa*) at room temperature gave the products *IIIa* (21%), *IVa* (9%), *VIa* (16%), *VIIa* (26%), *XV* (24%), i.e. also the 1,3-addition product *IIIa* which was not isolated in the case of N-butylindole. The structure was proved as in the above-given case. All the products obtained show a singlet in  $^1\text{H}$  NMR spectrum in the region  $\delta$  3.61–3.01 ppm for methyl group, which indicates that the indole heterocyclic skeleton was maintained. The cycloadducts type *XI* have the N—CH signal at  $\delta$  2.89 (ref.<sup>7</sup>). The derivative *XIII* formed by dehydrogenation of *XI* with chloranil in boiling xylene shows a signal of methyl group at  $\delta$  3.54 ppm and the absorption maximum in UV spectrum at 302 nm (ref.<sup>7</sup>). The compound *VIa* has  $\delta$  at 3.61 ppm, the 3-H singlet at 6.51 ppm, and  $\lambda_{\text{max}}$  at 289 nm. Structures of the compounds *IIIa*, *IVa*, and *VIIa* were proved by mass spectra and  $^1\text{H}$  NMR spectra. Again, the  $^1\text{H}$  NMR spectrum of *IVa* contains two doublets with coupling constant  $J = 6.0$  Hz at 5.69 ppm and 5.48 ppm (C—H and NH) which were proved by the decoupling experiment and addition of  $^2\text{H}_2\text{O}$ . The structure *VIIa* induces again the presence of 2-H singlet at low field at  $\delta$  9.57 ppm.



SCHEME 1

After the reaction of *I* with the parent indole (*IIC*) at 60°C, we could only isolate subsequent products of cycloaddition of *V*, i.e. *VIc* (34%) and *VIIc* (27%) and the product of self-reaction of nitron *I* (*XV*; 27%). Structure of compound *VIc* was assigned on the basis of the presence of aromatic multiplet at  $\delta$  6.86–8.16 ppm, the singlet at 6.60 ppm due to the 3-H proton signal in  $^1\text{H}$  NMR spectrum. In the  $^{13}\text{C}$  NMR spectrum,  $\text{C}_{(3)}$  is found at  $\delta$  42.8 and it exhibits a doublet in the spectrum by means of NOE experiment. The NH signal of  $^1\text{H}$  NMR spectrum in deuterioacetone is found at  $\delta$  9.98 ppm, in deuteriochloroform it is shifted to higher fields into the complex aromatic multiplet, and on addition of  $^2\text{H}_2\text{O}$  the signal disappears. The said shift is typical of NH signals of indole derivatives. The UV spectrum of *VIc* shows the last absorption band at 289 nm, for indole it is  $\lambda_{\text{max}} = 286$  nm. The IR spectrum contains absorption bands of carbonyl and NH groups at 1 690 and 3 469  $\text{cm}^{-1}$ , respectively. The nitron derivative *VIIc* exhibits in its mass spectrum the molecular ion  $\text{M}^{+}$  ( $m/z$  340) as well as the fragment  $m/z$  342 ( $\text{M}^{+} - \text{O}$ ), in its  $^1\text{H}$  NMR spectrum it shows a signal in low field at  $\delta$  9.46 ppm whose position is changed neither on heating nor on addition of  $^2\text{H}_2\text{O}$ . The signal is due to the 2-H proton of the 3-substituted indole derivative *VIIc*. A distinct bathochromic shift of *VIIc* as compared with *VIc* ( $\Delta = 45$  nm) indicates lengthening of the conjugated system, the  $\lambda_{\text{max}}$  value 334 nm being typical of nitron derivatives. It is noteworthy that the cycloaddition of *I* with indole (*IIC*) gave derivatives with maintained NH group in indole nucleus. From cycloaddition reactions of nitrile imines and indole it was only possible to isolate the 1 : 2 adduct formed by further 1,3-addition of nitrile imine to NH bond of indoline grouping in the cycloadduct *XI*. In our case, nitron *I* is a weaker electrophile than nitrile imine, it reacted also with furopyrrole without attacking the NH bond, and besides, the transient cycloadduct *V* is dehydrogenated to give indole grouping whereby the reactive enamine grouping is lost. If the reaction of *I* with indole was carried out at room temperature, the yields were lower: 22% *VIc* and 22% *VIIc*. The amount reacted with nitron *I* at 25°C (in brackets are the yields at 60°C) was in the case of N-butylindole (*IIB*) 35% (13%) by 1,3-cycloaddition and 12% (45%) by 1,3-addition, in the case of N-methylindole (*IIa*) 42% (30%), and in the case of indole (*IIC*) 44% (61%).

The summary of the given results indicates that the double bond  $\text{C}_{(2)}\text{C}_{(3)}$  behaves as dipolarophile to nitron *I*. The 1,3-dipolar cycloaddition is accompanied by competitive 1,3-addition, the formed 1,3-addition products with azomethine group cause dehydrogenation of transient cycloadduct *V*. The hydrogen formed in the reaction mixture reduces not only the 1,3-addition product but also the starting nitron *I*.

Tetrahydrocarbazole (*VIII*) did not react with nitron *I* even at 60°C. The reason is obviously in the steric hindrance due to methylene groups. 2-Phenyl- and 2-methylindoles only reacted with nitrile imines by 1,3-addition<sup>7</sup>, and 1,3-dimethylindole gave small amount of cycloaddition product. These results explain the non-reactivity of *VIII*.

Mass spectrum of compound *XV* contains molecular peak ( $m/z$  314) of slight relative intensity. By measurements at various temperatures it was found that this compound undergoes dehydrogenation already at small temperature increase of ionic source. Whereas at the temperature of the ionisation chamber  $100^{\circ}\text{C}$  the relative intensity ratio is  $(M^{+} - 2)/M = 1$ , it increases to 4 at  $120^{\circ}\text{C}$ . The basic peak in the spectrum is the ion with  $m/z$  104. Elemental composition of the ions was derived from the mass spectra (Table I).

The basic peak in the mass spectrum of compound *IIIa* corresponds to the ion with  $m/z$  233 which is formed by splitting off of  $\text{C}_6\text{H}_5\dot{\text{C}}\text{O}$  radical from molecular ion ( $m/z$  338). Subsequent splitting off of  $\dot{\text{C}}\text{H}_3$  and  $\dot{\text{C}}_6\text{H}_5$  radicals produces little intensive ions with  $m/z$  218 and 156, respectively. Analogous behaviour is shown also by compound *IIIb* with butyl substituent at nitrogen atom of indole nucleus, the only difference being in that the loss of  $\text{C}_6\text{H}_5\text{CO}$  radical from the molecular ion is followed by elimination of neutral butene molecule to give the ion with  $m/z$  219. The molecular ion with  $m/z$  354 is present with small relative intensity (6.5%) in spectrum of compound *VIIa*. Analogous fragmentation is also encountered with the molecular ion ( $m/z$  396) of compound *VIIb* with butyl substituent at nitrogen of the indole nucleus. The presence of alkyl group is manifested, in this case, by splitting off of neutral butene molecule from the basic ion of the spectrum  $m/z$  275 (100%)  $\xrightarrow{*}$   $m/z$  219 + 56. In the mass spectrum of compound *IVb* the molecular ion is not observed or its intensity is negligible. In this case we determined the molecular mass indirectly by measuring metastable transitions in the first pole-free region of the apparatus. Unambiguously proved was the transition  $382 \xrightarrow{*} 277 + 105$  corresponding to loss of  $\text{C}_6\text{H}_5\text{CO}$  radical. However, the spectrum contains a ion with  $m/z$  380 formed by dehydrogenation of the compound in ionic source of the mass spectrometer. Composition of this ion was derived from measurement of its exact mass (with the accuracy  $\Delta m = 0.00094$ ), whereby elemental composition of molecular ion  $\text{C}_{26}\text{H}_{26}\cdot\text{N}_2\text{O}$  could be determined indirectly.

TABLE I

Composition of some ions of a sample of compound *XV*

$m/z$	Measured mass	Composition
314	314.1409	$\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}$
312	312.1267	$\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}$
209	209.0854	$\text{C}_{14}\text{H}_{11}\text{NO}$
105	105.0528	$\text{C}_7\text{H}_5\text{O}$
104	104.0494	$\text{C}_7\text{H}_6\text{N}$

## EXPERIMENTAL

The melting point are not corrected. The IR spectra were measured in the region  $700-3800\text{ cm}^{-1}$  using a UR-20 spectrophotometer (Zeiss, Jena) with 0.6 mm NaCl cell and saturated chloroform solutions. The  $^1\text{H}$  NMR spectra were measured in deuteriochloroform, if not otherwise stated, using a BS-487 apparatus (80 MHz, Tesla Brno),  $\delta$  scale, and tetramethylsilane as internal standard. The  $^{13}\text{C}$  NMR spectra were measured with a Jeol FX-100 apparatus in deuteriochloroform. The mass spectra were measured with an MS 902 S apparatus (AEI Manchester) with direct inlet system and 70 eV electron energy. The UV spectra were measured with a UV VIS spectrophotometer in methanol. The reaction course and purity of the substances were checked by TLC with Silufol plates (UV<sub>254</sub> detection, detection with iodine vapours). The column chromatography of the vacuum-concentrated reaction mixtures was carried out on silica gel with cyclohexene-ethyl acetate (6:1 to 1:1) as eluents, the products *VIIa,b,c* were obtained by elution with methanol. *N*-Butyl- and *N*-methylindoles were obtained by reactions of indole and the corresponding alkyl iodide with phase-transfer catalysis (benzyltriethylammonium chloride)<sup>15</sup>. The products were separated from unreacted indole by column chromatography (SiO<sub>2</sub>, cyclohexane-ethyl acetate 7:1). The reactions of indole derivatives with nitronc *I* were carried out in dry toluene under nitrogen at room temperature or at 60°C.

Reaction with *N*-Methylindole

The mixture of 2.25 g (10 mmol) *I*, 2.7 g (20 mmol) *N*-methylindole, and 30 ml benzene was left to stand at room temperature 40 days to give the following compounds:

*IIIa*: 0.70 g, 21%, m.p. 163°C. For  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}$  (338.4) calculated: 81.63% C, 5.36% H, 8.28% N; found: 81.69% C, 5.41% H, 8.06% N.  $^1\text{H}$  NMR spectrum: 8.55–8.72 (m, 1 H, aromatic proton), 6.82–7.87 (m, 13 H, aromatic protons), 3.69 (s, 3 H, N—CH<sub>3</sub>). UV spectrum:  $\lambda_{\text{max}}$  249 nm (log  $\epsilon = 4.41$ ), 313 nm (log  $\epsilon = 4.28$ ). IR spectrum:  $\nu(\text{CO})$  1 672  $\text{cm}^{-1}$ .

*VIa*: 0.55 g, 16%, m.p. 138–140°C. For  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2$  (354.4) calculated: 77.95% C, 5.12% H, 7.91% N; found: 77.72% C, 5.05% H, 8.08% N.  $^1\text{H}$  NMR spectrum: 6.86–8.15 (m, 14 H, aromatic protons), 6.51 (s, 1 H, 3-H), 3.61 (s, 3 H, N—CH<sub>3</sub>). UV spectrum:  $\lambda_{\text{max}}$  289 nm (log  $\epsilon = 4.20$ ).

*XV*: 0.45 g, 28%, m.p. 140–141°C.  $^1\text{H}$  NMR spectrum: 4.91 (s, 1 H, C—H), 6.50–7.95 (m, 17 H, aromatic and CH=N— protons).  $^{13}\text{C}$  NMR spectrum: C<sub>(1)</sub> (152.63), C<sub>(2)</sub> (136.14), C<sub>(3)</sub> (129.35), C<sub>(4)</sub> (128.53), C<sub>(5)</sub> (128.12), C<sub>(6)</sub> (127.53), C<sub>(7)</sub> (120.63), C<sub>(8)</sub> (111.91), C<sub>(9)</sub> (107.76), and C<sub>(10)</sub> (81.84). UV spectrum:  $\lambda_{\text{max}}$  247 nm (log  $\epsilon = 4.32$ ). IR spectrum: 1 598  $\text{cm}^{-1}$  (C=C), 3 325  $\text{cm}^{-1}$  br, and 3 568  $\text{cm}^{-1}$  OH vibrations.

*IVa*: 0.3 g, 9%, m.p. 1931–95°C. For  $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}$  (340.4) calculated: 81.15% C, 5.92% H, 8.23% N; found: 81.42% C, 5.80% H, 8.31% N.  $^1\text{H}$  NMR spectrum: 8.35–8.46 (m, 1 H, aromatic proton), 6.62–7.77 (m, 13 H, aromatic), 5.69 (d,  $J = 6.0$  Hz, 1 H, C—H), 5.48 (d,  $J = 6.0$  Hz, 1 H, N—H), 3.70 (s, 3 H, N—CH<sub>3</sub>). UV spectrum:  $\lambda_{\text{max}}$  248 nm (log  $\epsilon = 4.50$ ), 308 (log  $\epsilon = 4.25$ ). IR spectrum:  $\nu(\text{CO})$  1 654  $\text{cm}^{-1}$ ,  $\nu(\text{NH})$  3 400  $\text{cm}^{-1}$ .

*VIIa*: 0.9 g, 26%, m.p. 213–215°C. For  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2$  (354.4) calculated: 77.95% C, 5.12% H, 7.91% N; found: 77.84% C, 5.10% H, 7.74% N.  $^1\text{H}$  NMR spectrum: 9.57 (s, 1 H, 2-H), 6.92 to 7.85 (m, 14 H, aromatic), 3.81), 3.81 (s, 3 H, N—CH<sub>3</sub>). UV spectrum:  $\lambda_{\text{max}}$  265 nm (log  $\epsilon = 4.40$ ), 338 nm (log  $\epsilon = 4.28$ ). IR spectrum:  $\nu(\text{CO})$  1 679  $\text{cm}^{-1}$ .



## Reaction with N-Butylindole

The mixture of 2.25 g (10 mmol) *I*, 3.45 g (20 mmol) N-butylindole, and toluene was left to stand at room temperature 21 days to give the following compounds:

*VIb*: 0.35 g, 9%, m.p. 116–118°C. For  $C_{26}H_{24}N_2O_2$  (396.5) calculated: 78.76% C, 6.10% H, 7.07% N; found: 78.91% C, 6.15% H, 7.38% N.  $^1H$  NMR spectrum: 6.86–8.11 (m, 14 H, aromatic), 6.46 (s, 1 H, 3-H), 3.96 (t,  $J = 6.0$  Hz, 2 H, N—CH<sub>2</sub>), 0.75–1.90 (m, 7 H, —CH<sub>2</sub>CH<sub>2</sub>·CH<sub>3</sub>). UV spectrum:  $\lambda_{max}$  287 nm (log  $\epsilon = 4.15$ ). IR spectrum:  $\nu(CO)$  1 691  $cm^{-1}$ .

*IVb*: 0.46 g, 12%, m.p. 140–141°C. For  $C_{26}H_{26}N_2O$  (382.5) calculated: 81.64% C, 6.85% H, 7.32% N; found: 82.02% C, 6.76% H, 7.27% N.  $^1H$  NMR spectrum: 6.61–8.02 (m, 14 H, aromatic), 6.32 (d,  $J = 3.8$  Hz, 1 H, C—H), 4.93 (d,  $J = 3.8$  Hz, 1 H, NH), 3.97 (t,  $J = 6.0$  Hz, 2 H, N—CH<sub>2</sub>), 0.75–1.80 (m, 7 H, —CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). UV spectrum:  $\lambda_{max}$  248 nm (log  $\epsilon = 4.49$ ), 309 nm (log  $\epsilon = 4.26$ ). IR spectrum:  $\nu(CO)$  1 692  $cm^{-1}$ ,  $\nu(NH)$  3 408  $cm^{-1}$ .

*XV*: 0.8 g, 50%.

*VIIb*: 1.0 g, 26%, m.p. 175–177°C. For  $C_{26}H_{24}N_2O_2$  (396.5) calculated: 78.76% C, 6.10% H, 7.07% N; found: 78.68% C, 5.95% H, 7.09% N.  $^1H$  NMR spectrum: 9.62 (s, 1 H, 2-H), 6.93 to 7.86 (m, 14 H, aromatic), 4.23 (t,  $J = 7.0$  Hz, 2 H, N—CH<sub>2</sub>), 0.90–2.03 (m, 7 H, —CH<sub>2</sub>CH<sub>2</sub>·CH<sub>3</sub>). UV spectrum:  $\lambda_{max}$  263 (log  $\epsilon = 4.34$ ), 338 nm (log  $\epsilon = 4.25$ ). IR spectrum:  $\nu(CO)$  1 675  $cm^{-1}$ .

Dehydrogenation of *IVb*

The mixture of 0.4 g (1 mmol) *IVb*, 0.6 g (2.6 mmol) DDQ, and 20 ml benzene was heated at 60°C 3 h. The mixture was worked up according to ref.<sup>3</sup> to give 0.30 g (75%) *IIIb*, m.p. 114–115°C. For  $C_{26}H_{24}N_2O$  (380.5) calculated: 82.07% C, 6.36% H, 7.36% N; found: 82.20% C, 6.20% H, 7.33% N.  $^1H$  NMR spectrum: 8.57–8.70 (m, 1 H, aromatic), 6.81–7.97 (m, 14 H, aromatic), 4.06 (t,  $J = 7.0$  Hz, 2 H, N—CH<sub>2</sub>), 0.83–1.88 (m, 7 H, —CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). UV spectrum:  $\lambda_{max}$  257 nm (log  $\epsilon = 4.40$ ), 313 (log  $\epsilon = 4.38$ ).

## Reaction with Indole

The mixture of 2.25 g (10 mmol) *I*, 1.17 g (10 mmol) indole, and 30 ml benzene was heated at 60°C 16 h to give the following compounds: *XV* (0.53 g, 27%), *VIc* (1.15 g, 34%), m.p. 217 to 218°C. For  $C_{22}H_{16}N_2O_2$  (340.4) calculated: 77.63% C, 4.74% H, 8.23% N; found: 78.01% C, 4.83% H, 8.14% N.  $^1H$  NMR spectrum ( $C^2H_3COC^2H_3$ ): 9.98 (s, 1 H, NH), 6.86–8.16 (m, 14 H, aromatic), 6.60 (s, 1 H, 3-H). UV spectrum:  $\lambda_{max}$  281 nm (log  $\epsilon = 4.18$ ), 289 nm (log  $\epsilon = 4.12$ ). IR spectrum:  $\nu(CO)$  1 690  $cm^{-1}$ ,  $\nu(NH)$  3 469  $cm^{-1}$ .

*VIc*: 0.90 g, 27%, m.p. 227–229°C. For  $C_{22}H_{16}N_2O_2$  (340.5) calculated: 77.63% C, 4.74% H, 8.23% N; found: 77.41% C, 4.62% H, 8.08% N.  $^1H$  NMR spectrum (hexadeuteriodimethyl sulphoxide): 9.46 (s, 1 H, 2-H), 6.83–7.80 (m, 15 H, aromatic and NH). UV spectrum:  $\lambda_{max}$  266 nm (log  $\epsilon = 4.66$ ), 334 nm (log  $\epsilon = 4.57$ ).

The authors are indebted to Mrs M. Somorovská, Mrs L. Livařová, Mrs E. Sýkorová, Mrs S. Markusová, and Mrs H. Hroboňová for technical assistance, spectral measurements, and elemental analyses.

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Translated by J. Panchartek.